Green synthesis, characterization and photocatalytic activity of inorganic semiconductors@g-C_3N_4 heterojunction nanocomposites under solar light illumination

Abstract of Thesis

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Abstract

This thesis deals with the studies based on the synthesis and characterization of inorganic semiconductors@g-C_3N_4 heterojunction nanocomposites such as SnO_2:Zn@g-C_3N_4, Fe:MoO_3@g-C_3N_4 , Cu doped SnO_2@g-C_3N_4 and MoO_3:Cu@g-C_3N_4 using aqueous extracts of *Murraya paniculata* leaves. The fabricated heterojunction nanocomposites were characterized using analytical techniques such as UV-visible spectroscopy, FT-IR spectroscopy, XRD, FE-SEM, EDX, TEM, XPS and photocurrent response analyses. The photo-assisted catalytic property of the synthesized heterojunction nanocomposites analysed against the degradation of toxic dyes was investigated. The mineralization of toxic pollutants was analysed via LC-MS, and COD analysis.

The first chapter includes a brief discussion of nanomaterials, classification of nanomaterials, synthetic approaches, their application in various fields, literature review, research gap identification, objectives and plausible outcomes of the work.

The second chapter includes a brief discussion of techniques and processes involved in the characterization of fabricated nanomaterials and methodology used in photocatalytic activity and photoelectrochemical water splitting for H_2 generation

In the third chapter, SnO_2:Zn@g-C_3N_4 heterojunction nanocomposite has successfully been synthesized via a green synthesis method using *Murraya paniculata* leaves extract. Materials were characterized by X-ray photoelectron spectroscopy (XPS), FTIR, XRD, BET, HRTEM, FESEM, EDAX, and UV-visible spectrophotometer. XRD and HRTEM results revealed the formation of highly crystalline and small sized particles having mean grain size of 4.4 and 4.9 nm for SnO_2:Zn and SnO_2:Zn@g-C_3N_4 respectively and interplanar spacing of 0.333 nm. The 2-D sheeted structure of g-C_3N_4 acts as a translucent layer that captures and provide a considerable extent of self-agglomeration on the underlying sphere shaped SnO_2:Zn NPs which results in excellent charge flow which eventually results in enhanced photocatalytic degradation performance of the synthesized heterojunction. The XPS analysis verifies the presence of Sn, Zn, O, C, and N in the synthesized heterojunction SnO_2:Zn@g-C_3N_4. The UV-Visible and photoluminescence spectra helped to demonstrate the effective inhibition of excitons annihilation within the heterojunction nanocomposite. The heterojunction shows an excellent photodegradation efficiency of 93.84% in the process of photodegradation of dye Malachite green (MG). Effect of pH, catalyst dose

on photodegradation and the recyclability were also investigated. The kinetic plots were used to calculate the rate constant which shows the nature of a pseudo first order reaction with a rate constant of 0.299 min^{-1}. Trap experiments were conducted to confirm the role of h^+ and $O_2^{\bullet-}$ as active species.

Fourth chapter reports synthesis of a heterostructure comprised of Fe doped MoO_3 (Fe:MoO_3), anchored on a g-C_3N_4 as a photocatalyst (Fe:MoO_3/g-C_3N_4), employing a sonication supported green synthesis method with the aid of *Murraya paniculata* leaf extract. We explored structural, morphological, and surface characteristics using various analytical techniques, including X-Ray diffraction (XRD), Fourier transform infrared (FTIR) spectroscopy, UV–visible spectroscopy, Field emission scanning electron microscopy (FE-SEM) and High-resolution transmission electron microscopy (HR-TEM), X-Ray photoelectron spectroscopy, and BET for a comprehensive surface analysis. The outcomes highlighted the exquisitely oriented and interconnected arrangement of MoO_3 nano rods ensconced within a piled layer of g-C_3N_4. The XRD patterns unveiled the coexistence of g-C_3N_4 and Fe:MoO_3 within the heterojunction structure. FESEM and HRTEM image analysis of Fe:MoO_3/g-C_3N_4 heterojunction reveals a g-C_3N_4 nanosheet wrapping the Fe:MoO_3 nanoparticles with the formation of nanorods of MoO_3 with an average thickness of 9.46 nm containing circular Fe nanoparticles with a mean diameter of 8.97 nm. This intricate configuration resulting in a decrease of the size of the nanoparticle caused by effective sonication-supported green modulation configuration facilitated an optimized charge flow, contributing to the elevated photo assisted catalytic performance of the heterojunction. The Fe:MoO_3/g-C_3N_4 semiconductor heterojunction exhibited a considerable surface area and pore volume, inherently amplifying the sites of the activity on the surface and thereby enhancing photoactivity. As opposed to both g-C_3N_4 and the Fe:MoO_3 nanoparticles, the Fe:MoO_3/g-C_3N_4 semiconductor heterojunction showcased enhanced photocatalytic effectiveness in the degradation of dye Crystal violet (CV). Under optimized circumstances, the photo assisted degradation of dye CV by the semiconductor heterojunction adhered to pseudo-first-order kinetics. The active species responsible for the photo assisted degradation process is identified as $^{\bullet}O_2^-$. These findings not only emphasize the enhanced efficacy of the developed semiconductor heterojunction but also reveal its potential for addressing the

environmental challenges posed by dye CV contamination through prolonged and efficient photocatalytic remediation practices. A marked improvement in both photo assisted catalytic and photoelectrochemical (PEC) water splitting activities under visible light exposure was showcased. The augmented performance of the Fe:MoO_3/g-C_3N_4 semiconductor heterojunction in photodegradation and PEC water splitting activities can be attributed to the extended absorption of visible light. Additionally, the synergistic influence of g-C_3N_4, contributes positively to the separation of charges and expedites the transfer efficiency of photogenerated charge carriers. This synergy enhances the overall effectiveness of the nanoparticles in harnessing visible light for efficient water-related processes.

In the chapter fifth, a photocatalyst consisting of Cu doped SnO_2 nanocomposite supported onto g-C_3N_4 using green synthesis method with the assistance of *Murraya paniculata* leaves extract has been prepared. To know about the structural, morphological chemical composition of the synthesised heterojunction several techniques of characterization techniques were employed such as XPS, XRD, BET, HRTEM, FESEM, EDAX and UV-Vis spectra. XRD results shows the spherical shape of the particles with the mean grain size of 2.18 and 2.14 nm for Cu doped SnO_2 and Cu doped SnO_2/g-C_3N_4 respectively. HRTEM results reveal that the fabricated Cu doped SnO_2 shows formation of very small size spherical nanoparticles. The heterojunction Cu doped SnO_2/g-C_3N_4 showed 2-D sheeted structure of g-C_3N_4 which acts as a translucent layer that captured sphere shaped Cu doped SnO_2 NPs. The XPS analysis verifies the existance of Sn, Cu, O, C and N in the synthesised heterojunction. The UV-Visible spectra helped to demonstrate the effective inhibition of plasmonic exciton annihilation within the heterojunction nanocomposite. When exposed to solar light, the designed nanocomposite heterojunction exhibited superior photocatalytic activity in the degradation of MG compared to undoped g-C_3N_4 and Cu doped SnO_2 binary nanocomposite. Additionally, the impact of physical attributes such as catalyst dosage and pH on MG photo-degradation was investigated, and the recyclability of the synthesized heterojunction was tested for up to 4 cycles. Radical scavenging studies indicated that $^{\bullet}O_2^-$ radicals were the principal species accountable for the degradation of MG by the nanocomposite heterojunction. The dye MG photodegraded with pseudo-first order kinetics. The excellent photocatalytic performance and recyclability of nanocomposite can be attributed to its greater

surface area, improved separation efficiency of excited e^--h+ pairs and superior absorption of visible light.

In the sixth chapter, we have shown a heterojunction semiconductor of MoO_3:Cu in conjunction with g-C_3N_4 was fabricated using a green synthesis approach facilitated by leaves extract of *Murraya paniculata*. Numerous methods of characterisation, including XPS, FTIR spectroscopy, XRD, BET, HR-TEM, FE-SEM, EDAX, and UV-visible spectrophotometry were employed to analyze the materials. The results from XRD and HRTEM indicated the highly crystalline nanoparticles with a mean particle size of 5.42 nm for MoO_3 nanomaterials with doping of 5.62 nm Cu particles. The two-dimensional g-C_3N_4 sheeted structure acted as a translucent layer, facilitating self-assembly on the spherical MoO_3:Cu nanoparticles, thereby promoting efficient charge flow and enhancing the photodegradation capability of the heterojunction semiconductor. XPS analysis confirmed the presence of Mo, Cu, N, O, and C in the fabricated heterojunction. UV-Visible and PL spectra demonstrated the efficient suppression of exciton annihilation in the heterojunction semiconductor. Remarkably, the heterojunction exhibited a high photocatalytic degradation performance of 97% for the photodegradation of Crystal violet (CV) dye. Additionally, the effects of pH and dose of catalyst on photodegradation, as well as the recyclability of the catalyst, were evaluated. Kinetic analysis revealed a pseudo first-order reaction with 0.617 min^{-1} rate constant, while scavenger experiments confirmed the involvement of h^+ and $^{\cdot}O_2^-$ as active species in the degradation process**.**

In the seventh chapter, the summary of the research work and the future aspects have been presented.

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